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PART VI: Miscellaneous

Chapter 14

SOYBEAN DERIVED FUEL LIQUIDS AS ADDITIVES FOR MIDDLE DISTILLATE TRANSPORTATION FUELS

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Abstract: Biodiesel liquids are increasingly being used as blending stocks with middle distillate ground transportation fuels or as a fuel itself. However, an upper limit of 20% biodiesel is common for a soy derived biodiesel blending stock with petroleum diesel fuels. It is important for operational consideration to look at the many problems this could present. Among the more important considerations are storage stability, filterability, temperature ranges, fuel compatibility, oxidative stability, and induced instability reactions. We compare the soy methyl esters to the untreated soy cooking oil for compatibility with petroleum fuels.

Key words: Biodiesel, Soybean fuels, Middle distillate, Methyl esters, Instability

1. INTRODUCTION

It is environmentally enticing to consider replacing or blending petroleum derived middle distillate fuels with biofuels for many reasons. Major considerations include the soaring world-wide price of petroleum products, especially diesel fuel and home heating oil, the toxicity of the petroleum-derived fuels and the environmental damage that leaking petroleum tanks can cause. For these reasons, it has been suggested that domestic agricultural renewable energy sources be considered as replacements, or at the least, as blending stocks for middle distillate fuels. If recycled soy restaurant cooking oils could be employed for this purpose, this would represent a further environmental advantage. Renewable plant sources of energy tend to be less toxic than their petroleum counterparts. This is an important consideration when tank leakage occurs. In proposing such a replacement, considerations must be given to the many problems that could arise. Problems to be studied include fuel storage stability, fuel solubility, oxidative stability, and seawater stability.

Truck fleet operators are one of the largest consumers of middle distillate fuels and this has ramifications throughout the fuel market especially in the winter months when home heating oil competes with diesel for limited refinery capacity. Many schemes have been proposed to decrease the nation's dependence on imported foreign crude oil. Most non-renewable sources, such as used automobile and truck tires or consumer plastic residues, produce products that require a great amount of additional processing to be useful. Renewable sources including plants, i.e., corn, soybeans or other vegetable oils, provide a viable resource as long as they can be produced and refined in suitable quantities. Of these plant derived materials, soybeans provide the most oil, up to 20% by weight, and the oil produced is cheaper than that of any other plant source, 17-20 cents/pound.

Diesel fuel specifications are very restrictive as to the quality of the product and the additives permitted. It is thus with great care that additives are considered. Important considerations in the use of additives include fuel solubility in the fuel at ambient and low temperatures, flash point, effect on cetane number and storage stability (ASTM, 1997). A critical point, however, is that the blending stock should not induce chemical instability in the fuel itself (Mushrush and Speight, 1998).

In the present research, we report on two different soybean derived blending stocks. Both were added in 10% and 20% blends with a known stable and then a known unstable petroleum middle distillate fuel. The blending stocks were obtained from different manufacturers and were commercially available. We examined the storage stability and the instability reactions. We looked at the fuel stability of these blends under both ambient and accelerated storage conditions.

2. EXPERIMENTAL

2.1 General Methods

Unless otherwise stated, chemicals were reagent grade and were obtained from commercial sources and used without additional purification.

2.2 Storage Stability Tests

The soy-fuel blends, 10% and 20%, were tested for storage stability and chemical instability reactions. They were tested by a gravimetric technique described in ASTM D5304-99a. A brief description of this method is: 100 mL sample of the blends in 125 mL borosilicate brown glass bottles were subjected to a 16 hour, 90°C time-temperature regimen at 100 psig overpressure of pure oxygen. After the reaction period, the samples were cooled to room temperature. The samples were filtered and the sediment determined by a gravimetric procedure.

2.3 Ambient Oxidative Stability Tests

The biodiesel liquids were subjected to a steady stream of ambient air for a one-week time period. The reaction was carried out in a one liter flask connected to an aspirator protected by a safety bottle. The air was filtered through a drying tube filled with anhydrous $CaSO_4$ with fiberglass plugs before passing through the soy derived liquid.

2.4 Soy Derived Biodiesel Fuel

Ag Environmental Products, 9804 Pflumm Road, Lenexa, KS 66215, supplied soy-derived biodiesel (SoyGold®) fuel A. This material was light yellow in color, had a boiling point greater than 400°F, negligible water solubility, a specific gravity of 0.88, a flashpoint of 425°F and a cetane number > 40. An eastern U.S. company distributed soy-derived biodiesel fuel B. It had a boiling point greater than 400°F, negligible water solubility, a specific gravity of 0.86, and a flashpoint greater than 300°F. No information on its cetane number was supplied. Both soy fuels, as supplied, had been converted to the methyl ester. No acidic material remained. This was confirmed by gc/ms as shown in Table 1.

2.5 Middle Distillate Fuels

All storage stability testing was done by ASTM D-5304. The petroleum middle distillate fuels were from our extensive inventory of well-characterized fuels. The stable fuel (No. 2 diesel) was an

American refined fuel that has been used as a stable fuel for comparison in our laboratory. This fuel yielded 0.2-mg of solids/100 mL fuel, and was therefore characterized as a very stable fuel. The unstable fuel was a Spanish refined number 2-diesel fuel. This fuel has historically been an unstable fuel, forming 2.5 mg of solids/100 mL fuel. This yield of solids ranks this fuel as very unstable.

3. RESULTS AND DISCUSSION

Petroleum derived diesel fuel has an average carbon number range of about C_{13} up to about C_{21} and a distillation range of about 150-400°C (300-750°F). To be acceptable by the military, a diesel fuel must meet many other specifications (ASTM, 1999b; MIL Spec., 1995). These include, for example, API gravity, flash point, pour point, water solubility, cetane number, acid number, total sulfur, filterability, and color test (ASTM, 1999b, 1999c). The soy-derived fuel meets many of these specifications such as flash point, API gravity, boiling point, cetane number and water solubility. These values were listed in the Experimental Section. The identity and concentration of the soy-derived methyl esters were confirmed by gc/ms analysis as shown in Table 1. No evidence of organosulfur or organonitrogen or other hetero-atomic compounds was detected. It was observed that only soy fuel (A) would pass the ASTM Color Test (ASTM, 1999b). Soy fuel (B) was a darker colored yellow liquid. It has been observed that this darkening may be related to degradation.

Table 1. Concentration in weight percent of the soy methyl esters in the biodiesel sample

Soy Methyl Ester	Carbon Number	Concentration in wt%
methyl linoleate	C_{18}	53
methyl oleate	C_{18}	24
methyl stearate	C_{18}	10
methyl palmitate	C_{16}	10
methyl linolenate	C_{18}	3

Table 2 illustrates the storage stability results for the soy-derived blending stocks. The storage stability ASTM-D5304 procedure yields results that are indicative of a one to two-year storage life for the fuel. Any fuel or fuel blend that gives gravimetric results of more than 2 mg of sediment/100 mL of fuel represents an unstable fuel. Table 2, depicts the results for diesel ground transportation fuels containing 10% and 20% blends of the methylated biodiesel soy liquids that were investigated. The results show that the soy fuel, SoyGold® (A), contained an antioxidant, which enhanced the stability for both the stable and unstable diesel fuels. For the 10% blends, 0.3 mg of solids/100 mL fuel formed and for the 20% blends, 0.2 mg of solids/100 mL fuel formed with the stable fuel. However, this was not the case for the second soy blending stock, (B), which contained no antioxidant. This soy liquid proved unstable for both the 10% and 20% blends. Results for the 10% blends yielded 3.0 mg of solids for the 10% soy blends and 4.6 mg of solids for the 20% soy blends.

The unstable petroleum derived diesel consistently has failed ASTM D-5304 storage test procedure with 2.5 mg of solids/100 mL of fuel. When this unstable fuel was blended with 20% soy liquid (A), a very dramatic change was noted.

Table 2. Storage stability of petroleum derived fuel and soy–petroleum and cooking oil-petroleum blends

Fuels	Gravimetric Sediment/100mL Fuel	
	Methyl Esters	Cooking Oil
Stable petroleum diesel	0.6	0.6
Unstable petroleum diesel	2.5	2.5
Fuel blends		
10% soy A – 90% stable diesel	0.3	2.7
20% soy A – 80% stable diesel	0.2	---
20% soy A – 80% unstable diesel	0.5	---
10% soy B – 90% stable diesel	3.0	4.4
20% soy B – 80% stable diesel	4.6	---
10% soy B – 90 % unstable diesel	3.0	---

This unstable fuel easily passed the storage stability test with only 0.5-mg of solids/100mL of fuel. This was the first time that we observed such a drastic change. Our laboratory has not noted this type of change with any other biofuel (corn, peanut, canola, etc.) blending stock. However, these observations were not duplicated in the case of soy-derived fuel liquid (B). When this biodiesel fuel liquid was blended with both petroleum derived fuels, the results were not very good. The stable petroleum diesel, both 10% and 20% soy (B) blends, failed the ASTM D-5304 Storage Stability test procedure. Both of these blends would thus lead to filter and injector plugging and other serious mechanical engine problems. The situation was even worse for the unstable petroleum fuel. The 10% soy (B) blend with the unstable petroleum diesel gave 3.0 mg of solids/ 100 mL and thus, unlike soy liquid (A) observations, the fuel remains unstable.

The presence of an antioxidant also had another effect on the two biofuel liquids studied in this work. It was observed that soy fuel (A) did not darken with exposure to light and air while soy fuel (B) darkened significantly. Several literature reports note that a color change may or may not be indicative of fuel oxidation reactions (Mushrush and Speight, 1995; Hiatt, 1971).

The same ASTM stability procedure was followed for another series of runs employing new soybean restaurant cooking oil. The results in Table 2 clearly show that this oil should not be used by large fuels users that buy fuels in bulk and store the fuel for any significant length of time. The 20% soy runs were not measured since the 10% soy oil did not pass the ASTM D-5304 stability procedure. Individual consumers that use a petroleum fuel cooking oil mixture immediately upon blending should not have any significant mechanical or operational problems.

4. CONCLUSION

Two soy bean derived blending stocks were obtained from two different manufactures. Both claimed to meet military specifications. Soy fuel A and Soy fuel B both appeared similar by GC and ^{1}H NMR. Soy blending stock A passed with ease all of the chemical tests while soy blending stock B failed all of the same procedures. Since both biodiesels had similar chemical and physical properties the differences in both storage stability and oxidative behavior may be attributed to the presence of antioxidants or to the presence of an ineffective antioxidant. New or filtered used soy derived cooking oils are satisfactory for individual consumers, but not large fleet operators that buy fuels in bulk and store them for any significantly length of time.

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